

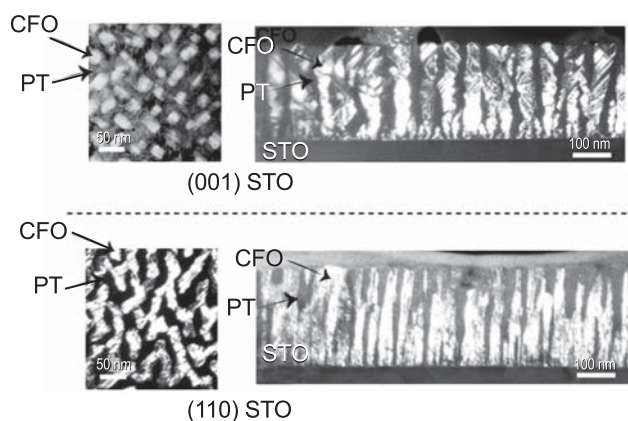
## Multifunctional Electronic Ceramics

*Materials which exhibit exploitable and coupled responses to multiple external fields (electric, magnetic, etc.) present entirely new design opportunities for multifunctional, miniaturized devices such as sensors or actuators. The goal of this project is to establish transferable engineering principles for multi- and single-phase electronic ceramics which exhibit a functional response by one constituent phase/subsystem that is generated by the response of another phase/subsystem to an external field.*

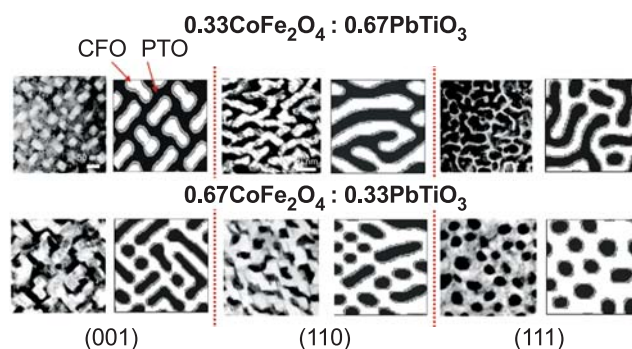
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The development of next-generation multifunctional devices now includes a search for materials exhibiting simultaneous magnetic, electronic, and/or photonic responses (*e.g.*, magnetic semiconductors, magnetic superconductors, multiferroics, etc.). Multiferroic materials display a coexistence of ferroelectric and ferromagnetic responses and have attracted particular interest for several novel device applications including memories, sensors, and actuators. Self-assembled, epitaxial heterophase nanostructures consisting of both ferromagnetic and ferroelectric phases represent one promising class of multiferroics. The strong magnetoelectric coupling obtained in these materials is attributed to the nanoscale distribution of the phases, which facilitates highly efficient elastic interactions and a strong magnetic response to an electric field (or vice versa) via magnetostriction and the piezoelectric effect. The same elastic interactions also control the self-assembly of the component phases, so that the architecture and the scale of the nanostructures can be predicted and controlled by manipulating the stress state of the film.

We analyzed the affect of stress conditions on the morphologies of epitaxial, self-assembled nanostructures



**Figure 1:** Plane view and cross-sectional images of the  $0.33\text{CoFe}_2\text{O}_4\text{-}0.67\text{PbTiO}_3$  nanostructures grown epitaxially on (001) and (110)  $\text{SrTiO}_3$ .



**Figure 2:** Plane view of  $\text{CoFe}_2\text{O}_4\text{-PbTiO}_3$  nanostructures grown epitaxially on (001), (110), and (111)  $\text{SrTiO}_3$ . For each composition and orientation, the experimentally observed structure is shown on the left and the simulation is shown on the right.

using  $\text{PbTiO}_3\text{-CoFe}_2\text{O}_4$  thin films. The two-phase nanostructures were grown on single-crystal  $\text{SrTiO}_3$ ; the strain conditions were varied by deposition on differently oriented substrates. Regardless of orientation, the nanostructures consisted of vertical columns of ferromagnetic  $\text{CoFe}_2\text{O}_4$  dispersed in a ferroelectric  $\text{PbTiO}_3$  matrix, or vice versa (Figure 1). However, the morphologies of these columns and their spatial arrangements exhibited a marked dependence on substrate orientation. Phase field modeling of these nanostructures, which assumed an equilibrium corresponding to the minimum of elastic and interfacial energies at a given phase fraction, succeeded in reproducing the morphological differences (Figure 2). The modeling confirmed that these differences are related to elastic anisotropy in the film. Our results, which demonstrate that the architecture of self-assembled multiferroic nanostructures can indeed be controlled by a careful choice of the stress conditions, open a tantalizing opportunity for the rational design of self-assembled, multifunctional nanostructures.

Research on bulk single-phase materials included phase equilibria studies of the  $\text{Bi}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-Nb}_2\text{O}_5$  and  $\text{Bi}_2\text{O}_3\text{-Mn}_2\text{O}_3\text{-Nb}_2\text{O}_5$  systems. Surprisingly, both systems feature extensive pyrochlore-type phase fields at compositions requiring mixing of the magnetic ions with far larger  $\text{Bi}^{3+}$  ions on the A-sites, in apparent violation of traditional substitutional rules. The pyrochlore phases exhibited relative permittivities  $\sim 150$ , and were readily deposited on Si as crystalline thin films using pulsed laser deposition. Although the multiferroic phase  $\text{BiFeO}_3$  was found to participate in ambient-pressure phase assemblages,  $\text{BiMnO}_3$  did not, and was not stabilized by the presence of  $\text{Nb}^{5+}$ .

### Contributors and Collaborators

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